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MS/MS BY TIME-RESOLVED MAGNETIC DISPERSION MASS SPECTROMETRY. (U)

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MS/MS BY TIME-RESOLVED MAGNETIC DISPERSION

MASS SPECTROMETRY

by

Christie G. Enke, John T. Stults, John F. Holland,

John D. Pinkston, John Allison and Jack T. Watson

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## MS/MS BY TIME-RESOLVED MAGNETIC DISPERSION MASS SPECTROMETRY

C.G. ENKE,<sup>1</sup> J.T. STULTS,<sup>2</sup> J.F. HOLLAND,<sup>3</sup> J.D. PINKSTON,<sup>4</sup> J. ALLISON,<sup>5</sup> and J.T. WATSON<sup>6</sup>

<sup>1,2,5</sup>Chemistry Dept., Michigan State Univ., E. Lansing, MI 48824 (U.S.A.)

<sup>3,4,6</sup>Biochemistry Dept., Michigan State Univ., E. Lansing, MI 48824 (U.S.A.)

### ABSTRACT

The modification of a magnetic sector mass spectrometer to provide measurement of ion flight time results in a novel instrument which can provide all the data presently obtained from tandem MS/MS instrumentation. The combination of ion momentum and velocity analysis provides unambiguous mass assignments for parent and daughter ions while flight time comparison establishes parent-daughter relationships. Data has been obtained from a modified LKB-9000 which demonstrates the feasibility of this technique. Suggestions for an upgraded instrument with automated scanning are made and the possibility of achieving full MS/MS data collection on the chromatographic time scale through the use of an integrating transient recorder is presented.

### INTRODUCTION

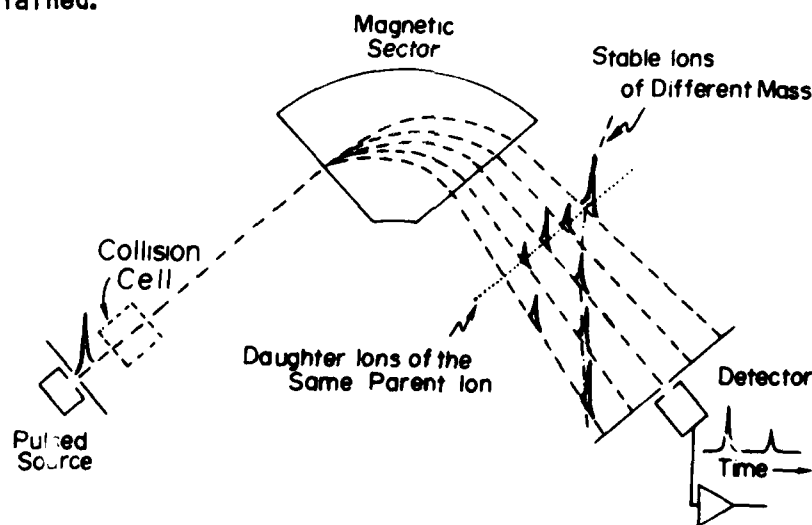
A new technique, based on measuring the flight time of ions in a magnetic sector mass spectrometer, can provide all the information currently obtained with tandem MS/MS instrumentation.<sup>1</sup> To implement this technique, the source of a magnetic sector mass spectrometer is modified to provide brief pulses of ions and time-resolved ion current detection is employed. Dispersion by the magnetic field allows only ions of a particular momentum to be detected while time-resolved detection provides an analysis of ion velocity. The product of the magnetic field strength  $B$  (proportional to the momentum,  $mv$ ) and the flight time  $t$  (proportional to  $1/v$ ) uniquely determines the  $m/z$  of a detected ion, independent of ion kinetic energy because ion velocity cancels out.

In tandem MS/MS the first mass filter selects a particular ion mass from the source after which it may undergo unimolecular or collision-induced dissociation (CID). The daughter ions from the fragmentation of the selected parents can then be mass analyzed by the second mass filter. Current MS/MS instrumentation is based on combinations of magnetic sector, electric sector, and quadrupole mass analyzers.<sup>2,3</sup> The mass selected by the analyzers can be scanned in such a way as to produce daughter, parent, or neutral loss spectra. The complete MS/MS data field is a three-dimensional plot of ion intensity vs

parent mass vs daughter mass and includes all the daughters of all the parents produced by the source.<sup>4</sup>

#### THE TIME DIMENSION IN MAGNETIC MASS SPECTROMETRY

Without time resolved detection, ion fragments formed between the source and the magnetic sector appear in the mass spectrum as "metastable" peaks at an apparent mass  $m^* = m_2^2/m_1$ , where  $m_1$  and  $m_2$  are the parent and daughter masses. Neither the daughter nor parent masses are uniquely determined by this relationship. The ion current can result from stable ions as well as daughter ions that have the same momentum. These normally superimposed contributions to the ion current can be sorted out by time resolution, however, since daughter ions resulting from post-acceleration fragmentation have nearly the same velocity as their parents.<sup>5</sup> As shown in Fig. 1, for any selected momentum, the stable ions will arrive first, followed by daughter ions of successively heavier parents. The masses of parent and daughter ions are determined by their  $Bt$  product and for each daughter ion, the mass of its parent is determined from the arrival time. Thus all the normal MS/MS data can be obtained.



Time-Resolved Magnetic Dispersion Mass Spectrometer

Fig. 1. Concept of time-resolved magnetic dispersion mass spectrometry. Reprinted with permission of the American Chemical Society from Ref. 1.

The occurrence of various types of ions as a function of  $B$  and  $t$  is illustrated in Fig. 2 for a mass spectrometer with an accelerating voltage of 3500 V, a sector radius of 0.2 m, and a flight path of 1.0 m. Stable ions

will occur along the line of unity slope. All daughters of a given parent will occur at the same flight time as their parent. Parent and daughter ions of a given mass fall on the hyperbola of constant  $Bt$  proportional to that mass. The energy spread of ions due to source or post-acceleration fragmentation processes will cause a spread of ion intensity along the constant mass line, but should not cause the mass resolution to be less than the resolution in the determination of  $Bt$ .

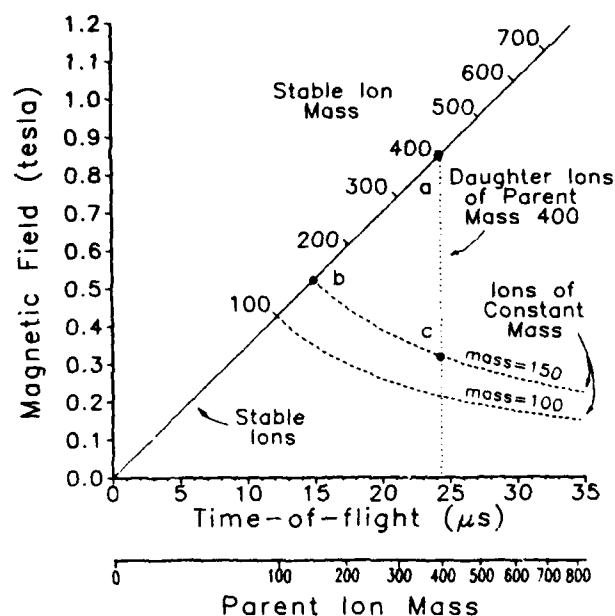


Fig. 2. Plot of field strength vs flight time for stable and daughter ions. Points a and b are for stable ions of  $m/z$  400 and 150. Point c is a daughter of  $m/z = 150$  from a parent of  $m/z$  400. Reprinted with permission of the American Chemical Society from Ref. 1.

#### EXPERIMENTAL

Time-resolved magnetic dispersion mass spectrometry has been demonstrated in our lab by very minor modifications to an LKB-9000 magnetic sector mass spectrometer. A square wave modulation was applied to the existing beam focussing plates to deflect the beam away from the sector except for an instant during the rising and falling edges of the square wave. Ion current was observed on an oscilloscope connected directly to the electron multiplier detector and triggered by the square wave source. For several compounds, various stable and daughter ions were observed and identified. For example, the molecular ion of 1,4-dioxane of  $m/z$  88 was observed to have a flight time of 13.0  $\mu$ s. At the appropriate field strength, a stable ion mass 38 was

observed with a flight time of 8.8  $\mu$ s. At that same field strength, a daughter ion formed by metastable decomposition was also observed. From its flight time of 13.0  $\mu$ s, the mass of its parent was determined to be 88, the molecular ion. From the combination of field strength and flight time, an unambiguous daughter mass of 58 could be assigned. This implementation has demonstrated the feasibility of this technique, but data collection at present is manual and tedious.

#### FUTURE IMPLEMENTATIONS

A boxcar integrator used as the detector amplifier will allow automatic collection of the entire data field. Linked scanning of the field strength and the sampled arrival time will provide daughter, parent, and neutral loss scans as in modern tandem MS/MS. Efficiency will be further improved through use of a pulsed rather than chopped source and through the addition of a collision cell. Arguments supporting the expectation of comparable sensitivity and improved mass resolution with respect to the normal magnetic sector mass spectrometer are presented elsewhere.<sup>1</sup>

The ultimate capability of time-resolved magnetic dispersion mass spectrometry will result when used with the integrating transient recorder currently under development in our laboratory. This system will be able to record all the ions transmitted in each pulse with a time resolution of 5 ns. Time spectra from ten to one thousand source pulses (occurring over a 400  $\mu$ s to 40 ms interval) will be averaged before spectral processing and storage. The ability to record all ion arrival times will allow the complete B vs t data field to be collected in a single sweep of the magnetic field strength. The goal of this implementation is to achieve complete MS/MS spectra on the time scale of chromatographic peaks for true GC/MS/MS. Only with this capability will the full power of MS/MS be available for screening analyses of complex mixtures.

#### SUMMARY

It has been demonstrated that through the minor modification of a magnetic sector mass spectrometer for time-resolved detection daughter ions can be distinguished from stable ions, the masses of both can be determined unambiguously and the data provided by conventional tandem MS/MS can be provided. A box-car integrator ion detection system could provide automated data collec-



tion and all the standard MS/MS scanning modes under appropriate computer control. With an integrating transient recorder, the complete time array could be recorded for each source pulse and give the complete MS/MS data field for each scan of the magnetic field strength. This extremely high data collection rate opens the possibility of full MS/MS on the chromatographic time scale.

#### REFERENCES

- 1 J.T. Stults, J.F. Holland and C.G. Enke, Anal. Chem., accepted for publication.
- 2 F.W. McLafferty, Science, 214 (1981) 280-287.
- 3 R.G. Cooks and G.L. Gilsh, Chem. Eng. News, 59 (1981) 40-52.
- 4 R.A. Yost and C.G. Enke, Anal. Chem., 51 (1979) 1251A-1264A.
- 5 R.G. Cooks, J.H. Beynon, R.M. Caprioli and G.R. Lester, Metastable Ions, Elsevier, New York, 1973, 59-60.

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